(12) UK Patent Application (19) GB (11) 2 062 615 A

(21) Application No 8032139
(22) Date of filing 6 Oct 1980
(30) Priority data
(31) 54/128378
55/006633
55/020624
(32) 4 Oct 1979
22 Jan 1980
22 Feb 1980
(33) Japan (JP)
(43) Application published
28 May 1981
(51) INT CL[3]
C03C 17/09
(52) Domestic classification
C1M 400 401 PX
(56) Documents cited
GB 1450123
(58) Field of search
C1M
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(54) **Preparing glass preform for optical transmission**

(57) A process for producing a glass preform for optical transmission comprises supplying a gaseous silicon compound, a gaseous nitrogen compound and an oxygen-containing gas as starting gases into a high temperature zone to effect a reaction in such a manner that an oxygen-silicon bond is initially formed and then a nitrogen-silicon bond is then formed to produce a SiOxNy glass. The SiOxNy glass is deposited as a transparent glass on a starting member to produce a nitrogen-doped silica glass, or alternatively is deposited on the starting member as fine particles which are then sintered to produce a nitrogen-doped silica glass.

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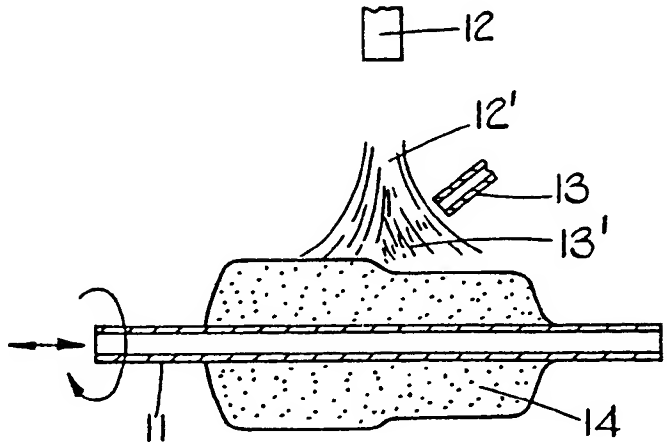

FIG. 1.

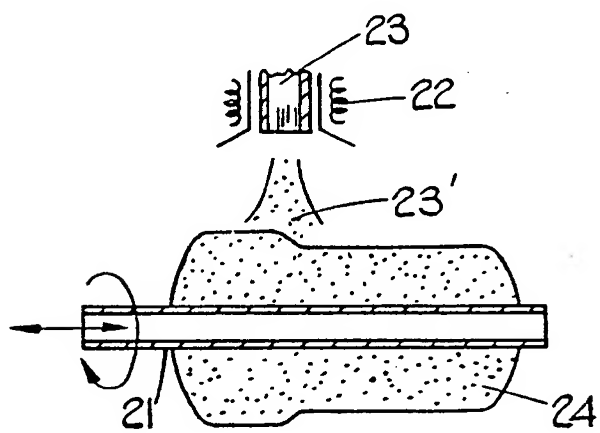

FIG. 2.

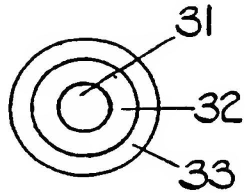

FIG. 3a.

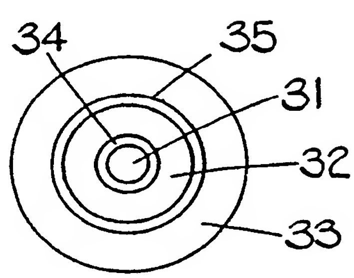

FIG. 3b.

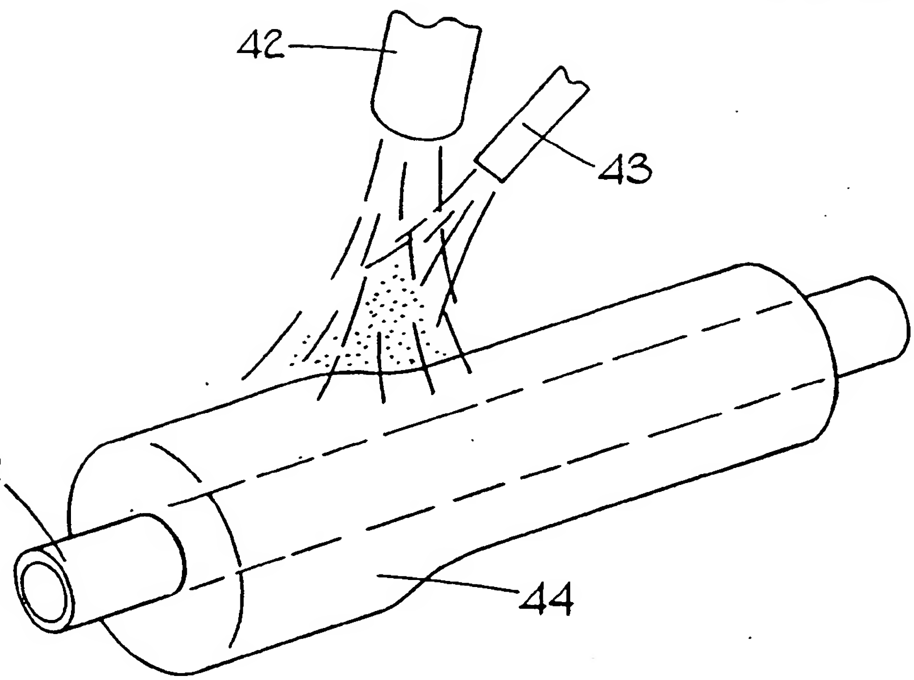

FIG. 4.

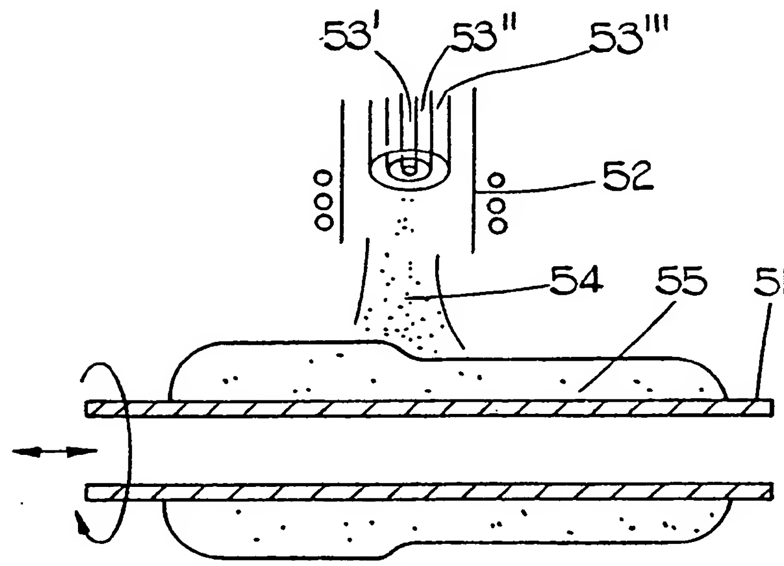

FIG.5.

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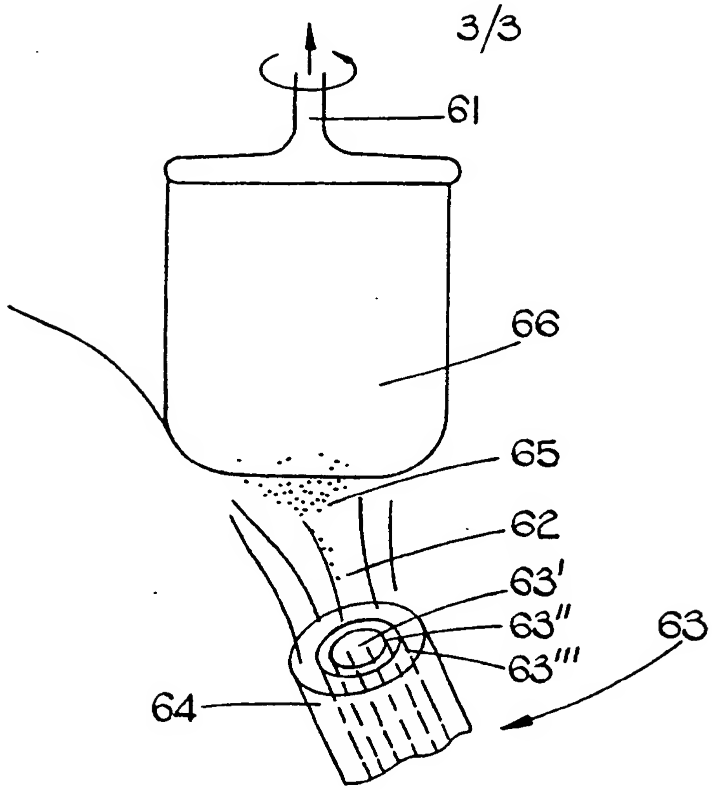

FIG. 6.

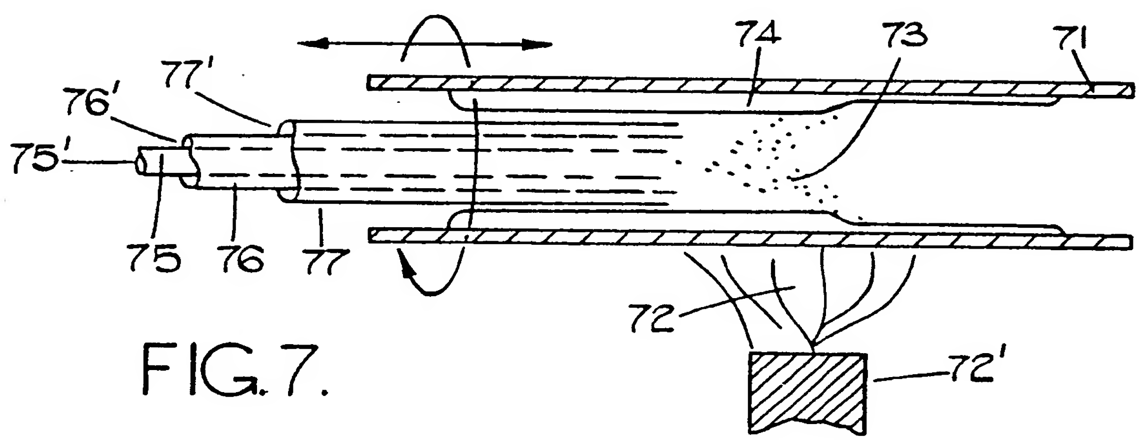

FIG. 7.

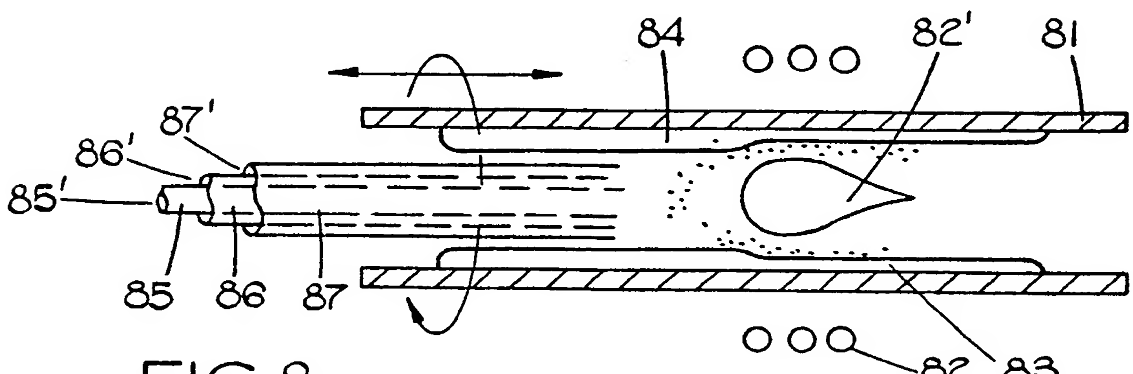

FIG. 8.

SPECIFICATION

A process for preparing a glass preform for optical transmission

This invention relates to a process for preparing a glass preform for production of an optical fiber.

Generally, a glass preform for optical transmission is required to have a predetermined distribution of refractive index in the radial direction of the glass rod, uniformity in the concentration and composition of ingredients, a low content of OH radicals and impurities comprising transition metals such as iron and copper, and a high light transmittance. As described in Japanese Patent Application (OPI) Nos. 6428/71, 5788/71, 10055/74 and 10056/74 (the term "OPI" as used herein refers to a "published unexamined Japanese Patent Application"), such a preform is conventionally produced by the MCVD process, the OVPD process or the VAD process from silica-based glass doped with a metal oxide to produce a high refractive index. However, although a silica-based glass doped with metal oxide has a high light transmittance, the dopant used is expensive.

As disclosed in Japanese Patent Application (OPI) Nos. 76538/74 and 87339/75, it is well known that metal oxide dopants can be replaced with fluorine or nitrogen either to increase or decrease the refractive index of glass, but this conventional method is not capable of producing stably silica-based glass containing a predetermined amount of nitrogen dopant. One of the articles that report the change in the refractive index of SiOxNy glass according to the amount of dopant nitrogen is A. K. Gaind and E. W. Hearn, "Physicochemical Properties of Chemical Vapor-Deposited Silicon Oxynitride from an SiH_4-CO_2—NH_3—H_2 System" in I. Electrochem. Sa.: Solid-State Science and Technology, Jan. 1978, pp. 139—145. One method for producing such SiOxNy glass is the chemical vapor deposition (CVD) process described in A. K. Gaind, G. K. Ackerman, V. J. Lucarini and R. L. Bratter, "Oxynitride Deposition Kinetics in an SiH_4—CO_2—NH_3—H_2 System" in I. Electrochem. Sa.: Solid-State Science and Technology, April, 1977, pp. 599—606. However, the primary purpose of this method is to deposit a stable film of SiOxNy on a silicon wafer, and the method aims at providing an SiOxNy film of good characteristics rather than forming it quickly. For this reason, the rate at which the film is formed in a given period of time according to this method is low. That is, the method produces a non-defective film with low concentrations of materials being supplied into a heterogeneous reaction system at relatively low temperature by way of contrast, in the production of a glass fiber for optical transmission, since the role of glass *per se* predominates over other components and also the glass is used in a large quantity, the rate of formation of a glass fiber must be at least a hundred times faster than that of the film of SiOxNy formed on the silicon wafer. The content of

$$\begin{array}{c} | \\ \text{—SiOH} \\ | \end{array}$$

radicals in a glass fiber for optical transmission should be minimized because their presence is the cause of absorption loss, particularly transmission loss in the range of long wavelengths, due to their vibration. However, in the conventional film making technique that uses NH_3 as one material, the formation of residual

$$\begin{array}{c} | \\ \text{—SiOH} \\ | \end{array}$$

radicals is unavoidable because of the presence of hydrogen.

On the other hand, Japanese Patent Application (OPI) No. 134134/79 discloses that a porous glass can be doped with nitrogen by subjecting the porous glass to heat treatment in ammonia, but such process is not satisfactory since the amount of nitrogen doped becomes extremely high.

One object of this invention is to provide a process for producing a glass preform suitable for making a glass fiber for optical transmission having low transmission loss, a parabolic distribution of refractive index in a radial direction to reduce optical signal distortion and having increased practical strength. Such glass preform is produced by making silica doped with a dopant comprising nitrogen alone or in combination with other dopants in the form of an oxide or by additionally making undoped silica or silica doped with fluorine.

A further object of this invention is to make fine particles of SiOxNy glass by supplying glass-making gases in such a manner that an Si—N bond of low chemical bond strength is formed.

Another object of this invention is to produce N-doped SiOxNy glass at a rate at least a hundred times faster than in the conventional CVD process. This object is achieved by performing a homogeneous reaction with a high concentration of a silicon compound at high reaction temperatures and either forming directly a transparent glass coating from the resulting powder of SiOxNy or sintering the resulting powder of SiOxNy to make a transparent glass product.

The present invention makes it possible to produce SiOxNy glass with or without using ammonia and includes the following three alternative procedures:—

[1] A process comprising making fine particles of SiOxNy glass using NH_3 and sintering the fine

particles to produce a transparent glass product, care being taken to reduce the amount of nitrogen dopant in the surface of the glass particles to provide a composition close to that of SiO_2 to thereby eliminate any residual air bubbles from the glass particles being sintered.

According to this process, the values of x and y of the SiOxNy are controlled by varying the amounts of nitrogen and oxygen dopants through changes in the ratio of NH_3 to oxygen-containing gas, such as NH_3/CO_2 or NH_3/NO_2, with a constant supply of silicon compounds such as $SiCl_4$, $SiHCl_3$ and SiH_4 (silicon halides, organic silicon compounds and silicon hydrides). In one embodiment, the heating source used is a combustion flame, a hot furnace, such as an electric furnace, or a plasma flame wherein the gas mixture supplied is surrounded by an inert gas or hydrogen. If the source of heating is the heat of the combustion reaction between H_2 or C_mH_n, such as C_3H_8, and oxygen, CO_2 and H_2O are produced in excess amount with respect to the silicon compound and NH_3, and most of the silicon compound reacts with these by-products to form SiO_2 rather than the intended SiOxNy doped with nitrogen and, therefore, some technique would be required for preventing SiO_2 formation.

[2] A process comprising forming and depositing SiOxNy as a transparent glass using NH_3, by supplying a gaseous silicon compound, ammonia, and oxygen and/or a gaseous oxygen compound into a combustion flame where the three gases react with each other to form fine particles (or soot) of SiOxNy glass, and a layer of the glass soot formed is directly deposited on a starting member in a molten state to thereby form nitrogen-doped silica glass.

[3] A process comprising making SiOxNy glass without using NH_3, wherein $SiCl_4$ gas which reacts with oxygen gas to form SiO_2 and NCl_3, NOCl, NO_2Cl or ClN_3 which generates nascent nitrogen are used as materials for making glass of high refractive index, and NO_x (e.g., NO, NO_2, N_2O, N_2O_5), CO_2 or O_2 which exhibits an oxidizing effect at high temperatures is used as an oxidizing gas. By using these gases, SiOxNy glass substantially free from residual

$$\begin{array}{c} | \\ -\text{SiOH} \\ | \end{array}$$

radicals is produced. If necessary, N_2F_2 or NF_3 can be used as the gas for generating nascent nitrogen.

The source of heating used in this invention is an energy source free from hydrogen, such as CO_2 laser, an anhydrous plasma flame or a combustion flame obtained by oxidizing $(CN)_2$, CS_2 or CCl_4. Alternatively, the presence of hydrogen can be avoided by applying heat indirectly to the reaction mixture through the wall of a silica tube. In either method, a gas mixture substantially free from

$$\begin{array}{c} | \\ -\text{SiOH} \\ | \end{array}$$

can be obtained.

Table 1 below illustrates various gases used to supply nitrogen. The table also shows the characteristics of these gases.

TABLE 1

Compound	m.p. (°C)	b.p. (°C)	State of Ordinary Temp.	Remarks
N_2F_2	−100		colorless gas	with odor
NF_2		−125		not available as pure form
NF_3	−216.6	−120	colorless gas	stable and not explosive
NCl_3	<−27	≦71	yellow oily liquid	explosive
ClN_3	−100	−15	colorless gas	little dangerous if mixed with N_2
NOCl	−64.5	−5.5	yellowish red gas	highly reactive
NO_2Cl	−31	5	yellowish to reddish brown gas	

According to this invention, the values of x and y of SiOxNy are controlled by varying the amounts of nitrogen and oxygen dopants through changing the relative proportions of Si-supply gas ($SiCl_4$), N-supply gas (NCl_3, NOCl, NO_2Cl, ClN_3, N_2F_2, NF_3, etc.), and O-supply gas (O_2, CO_2, NO_2, etc.), especially the ratio of N-supply gas to O-supply gas.

This invention achieves the mixing and reaction of these gases by means of a combustion flame or by making use of a partition wall composed of silica glass if such mixing and reaction should be performed only within the reaction system. Alternatively, the same object can be achieved by supplying these gases in a diluted form. It is to be understood that some gases do not need a partition wall or a sheathed nozzle.

In the present invention, $SiCl_4$ that reacts with oxygen gas to form SiO_2 or $SiF_4/SiCl_4$, $SiCl_4/COF_2$, CF_4, SF_6 or CCl_2F_2 that reacts with oxygen to form F-doped SiO_2 glass is used as a material for making glass of low refractive index, and NO_2, CO_2 or O_2 that exhibits oxidizing effect at high temperatures is used as an oxidizing gas. By using these gases, SiO_2 glass or F-doped SiO_2 glass substantially free from residual

$$\begin{array}{c} | \\ \text{—SiOH} \\ | \end{array}$$

radicals is produced. If necessary, N_2F_2 or NF_3 may be used as a gas for generating nascent fluorine.

In accordance with the process of this invention, a fiber having a clean and smooth surface free from origins of Griffice crack can be obtained by melt-spinning a preform coated with SiO_2 doped with Al_2O_3, TiO_2 or ZrO_2 that has a lower melting point and thermal expansion coefficient than pure SiO_2. The fiber also has great strength because it has residual compressive strain in the surface.

The conventional method for producing a glass preform for making an optical fiber is described hereunder. A mixture of a gaseous silicon compound such as SiH_4, $SiHCl_3$, $SiCl_4$ or SiF_4 (hydrogenated silicon compounds,organic silicon compounds and silicon halides), an oxygen-containing gas such as CO_2, NO_x or O_2, and a gas such as NH_3 that generates nascent nitrogen gives SiOxNy under heating at elevated temperatures following the reaction course indicated below:

$$SiH_4 + xCO_2 + yNH_3 \rightarrow SiOxNy + xCO + (2 + \frac{3}{2}y)H_2 \quad (1)$$

$$SiCl_4 + xCO_2 + yNH_3 \rightarrow SiOxNy + xCO + 4HCl + (\frac{3}{2}y - 2)H_2 \quad (2)$$

As mentioned above, these SiOxNy compounds

$$(SiO \text{ to } SiN\frac{4}{3})$$

are generally used to make a protective film in a semiconductor by applying a radio frequency plasma in vacuum (at lower temperature) or by the CVD process. According to one example of the reaction (1) for the CVD process achieving faster film formation, dilute materials are used (i.e., H_2: ~110 l/min., $NH_3 + CO_2$: ~2.3 l/min., SiH_4 (5% in H_2): ~10 cm³/min., ~200 cm³/min., 900—1,000°C) and the reaction temperature is as low as 800 to 1,200°C. In one example of the reaction (2), the production of Si_3N_4 is performed using $SiCl_4$ and NH_3 at a temperature between 1,000 and 1,500°C. According to such conventional method, it is not easy to make sufficient glass to meet the requirements for the production of a glass preform. According to this invention, the end products of the reactions (1) and (2) are formed in great quantities by supplying increased amount of a gaseous silicon compound and other materials at higher temperatures.

The invention will now be more particularly described with reference to the accompanying drawings in which:—

Figures 1 and 2 illustrate processes for producing a glass preform for optical transmission according to first and second embodiments respectively of the present invention,

Figures 3(a) and 3(b) are respective cross sectional views of nozzles for use in the process of the present invention,

Figure 4 illustrates the principle of operation of a process for producing a glass preform for optical transmission by a third embodiment of the present invention utilizing the outside vapor-phase deposition (OVPD) process,

Figure 5 is a schematic representation of a fourth embodiment of the invention in which a SiOxNy glass is produced by the outside vapor-phase deposition process wherein individual gases are supplied

into a plasma flame,

Figure 6 is a representation of a fifth embodiment in which a SiOxNy glass is produced by the vapor-phase axial deposition process wherein individual gases are supplied into an anhydrous flame such as CS_2—O_2 flame,

Figure 7 is a schematic representation of a sixth embodiment in which a SiOxNy (anhydrous) glass is produced by the modified chemical vapor deposition (MCVD) process, and

Figure 8 is a schematic representation of a seventh embodiment in which a SiOxNy (anhydrous) glass is produced by the plasmc chemical vapor deposition (PCVD) process.

In the drawings, the reference numerals 11 and 21 indicate starting members; 12 is a high frequency plasma torch; 12′ is a hot gas; 13 and 23 are nozzles; 13′ and 23′ are fine particles of glass; 14 and 24 are finely divided SiOxNy glass; 22 is a furnace; 31, 32 and 33 are gas outlets of nozzles; 34 and 35 are gas outlets of nozzles for producing gas curtains; 41 is a silica tube; 42 is a high frequency plasma torch; 43 is a nozzle; 44 is a nitrogen-doped silica glass; 51 and 61 are starting members; 71 and 81 are silica glass tubes as starting members; 52 and 82′ are plasma flame; 62 is a combustion flame; 72 is an oxygen-hydrogen flame; 53, 63, 75, 76, 77, 85, 86 and 87 are starting gas supply pipes; 54, 65, 73 and 83 are fine particles of SiOxNy glass; and 55, 66, 74 and 84 are deposited glass.

[1] Process for producing a transparent glass by making fine particles of SiOxNy glass using NH_3 as a starting gas and then sintering the particles:

Referring to Figure 1, in the process of said first embodiment of the invention, a starting member 11 in the form of a thin-walled silica tube (which may be reinforced with a graphite rod inserted in it) is rotated or reciprocated as shown, and a hot plasma flame 12′ of inert gas such as Ar or N_2 produced by a high-frequency plasma torch 12 is directed against the tube 11. As the hot inert gas issues from the torch, three gases, i.e., a gaseous silicon compound such as SiH_4, NH_3 and an oxygen-containing gas, are supplied through a nozzle 13 to be described hereunder, and the mixture of the three gases is heated with said hot inert gas 12 to produce SiOxNy 13′, which is deposited on the starting member as a coating of finely divided SiOxNy glass 14.

Referring to Figure 2, in the second embodiment a starting member 21 is rotated or reciprocated while glass-making gases supplied from a nozzle 23 are heated in a furnace 22 such as an electric furnace (using a platinum wire). As described hereunder, the construction of the nozzle 23 is such that an inert gas such as helium of nitrogen is supplied from an outer coaxial pipe to provide a separation between the air and the gases supplied from inner pipes. As a result of the high-temperature reaction, a coating of SiOxNy 23′ is formed on the starting member as a finely divided glass product 24.

In the reaction of the type used in this invention where high concentrations of gases are supplied at high temperature, for example, in a reaction under such conditions that SiH_4 and a mixture of NH_3 and CO_2 are supplied at rates of 100 cm^3/min and less than 10 l/min, respectively, at 1,000 to 1,500°C or $SiCl_4$ and a mixture of NH_3 and CO_2 are supplied at rates of less than 100 cm^3/min and less than 10 l/min, respectively, at 1,100 to 1,700°C, the individual gases are preferably separate from each other before they enter the reaction system. This can be achieved using the nozzle which is shown in Figure 3(a) and which comprises coaxial pipes 31, 32 and 33 through which separate gases are supplied. Examples of the combinations of gases to be supplied through the three pipes include the combination of a mixture of NH_3, H_2 and inert gas (to be supplied through the pipe 31), a mixture of a gaseous silicon compound, H_2 and inert gas (supplied through the pipe 32), and an oxygen-containing gas (through the pipe 33), as well as the combination of a mixture of a gaseous silicon compound, H_2 and inert gas (through the pipe 31), a mixture of NH_3, H_2 and inert gas (through the pipe 32), and an oxygen-containing gas (through the pipe 33). Another possible combination comprises a mixture of NH_3, gaseous silicon compound, H_2 and inert gas (supplied through the pipe 31) and an oxygen-containing gas (supplied through the pipe 33). In the last mentioned combination, the pipe 32 is omitted from the nozzle. It is to be emphasized here that the oxygen-containing gas should be supplied from an outer pipe to effect Si—N bonding to some extent before the formation of the Si—O bond. If the circumstances permit the use of a nozzle of complex construction, the gases mentioned above (those supplied from the central pipe mentioned first, next come those supplied from the intermediate pipe, and those supplied from the outer pipe mentioned last) may be supplied in portions rather than in a single stream. In this case, an oxygen-containing gas may be supplied through the central pipe.

Referring to Figure 3(b), the nozzle shown therein is designed to cater for the problem that gases having different properties may mix and react with each other right at the discharge end of the nozzle and form fine particles of glass that deposit on the tip of the nozzle to reduce the gas flow. This can be effectively prevented by providing a pipe 34 for generating a gas curtain between the pipes 31 and 32 of Figure 3(a) as well as a further pipe 35 provided for the same purpose between the pipes 32 and 33. Examples of effective curtain gases are those of high thermal conductivity such as helium and hydrogen that provide a uniform temperature distribution for the gases to be mixed subsequently in the reaction system. To change the refractive index by variation of the amount of nitrogen dopant (the more nitrogen dopant used, the higher the refractive index of SiOxNy), a gaseous silicon compound is supplied at a rate that is determined by the desired rate of glass formation, while the ratio of a mixture of NH_3 and an oxygen-containing gas to the gaseous silicon compound is held constant, and the ratio of NH_3 to the oxygen-containing gas is varied. This technique is advantageous in that it achieves uniform doping of

SiOxNy.

The above description is based on the production of a glass preform by the OVPD method (outside vapor-phase deposition method), but it is to be understood that the process of this invention can also be implemented by the MCVD method (modified chemical vapor deposition method) or VAD method. If necessary, the coating of finely divided SiOxNy glass deposited on a starting member by the method of this invention can be overlaid with a coating of finely divided SiO_2 glass with or without a fluorine dopant. To achieve this purpose, the reaction may be performed at a suitable temperature with the valve on the NH_3-supply line being closed or with a fluorine-containing gas being supplied into the NH_3-supply line or the gaseous silicon compound-supply line.

The resulting powder of SiOxNy of this invention is then sintered at about 1,450°C which is close to the temperature for sintering undoped SiO_2 glass. This sintering operation differs from the sintering of B_2O_3-, P_2O_5- or GeO_2-doped glass produced by the conventional MCVD method, OVPD method or VAD method in that it must be performed in an oxygen-free inert gas atmosphere or in vacuum or in a gas atmosphere containing elemental chlorine, such as Cl_2, NCl_3, ClN_3, or HCl, instead of oxygen, for example, a gas atmosphere of Ar + Cl_2, He + HCl, or He + Cl_2. This is because of the presence of oxygen at a temperature close to the sintering temperature results in oxidation of nitrogen. Individual fine particles of SiOxNy glass are preferably surrounded by a composition doped with only a small amount of nitrogen and hence close to that of SiO_2, because this results in the production of a sintered product completely free from air bubbles. To provide such a desired product, fine particles of SiOxNy are gradually heated to a temperature lower than the sintering point either in vacuum or an oxygen-free inert gas or chlorine gas, and thereafter, the particles are held in a dry oxygen gas to bring the composition of the superficial part of the particles close to that of SiO_2, followed by sintering in the atmosphere defined above. An effective method for this sintering is the conventional "zone sintering" technique. In this way a sintered, transparent glass preform is obtained wherein the content of nitrogen dopant increases to provide a higher refractive index as the radial distance from the center increases and which has an outer layer of low refractive index made of undoped pure silica or F-doped pure silica. The sintered preform obtained by the method illustrated in Figure 1 or Figure 2 is then freed of the starting member, and its inside surface is made smooth and clear by reaming, laser treatment, flame treatment, washing in hydrofluoric acid or any other conventional technique to provide a cylindrical glass product, which is optionally mounted on a glass lathe and drawn under heating to collapse the hollow part of the cylinder to make a preform rod. The resulting preform cylinder or rod is subjected to a surface treatment to provide a smooth and clean outer surface, and is supplied into a high-frequency induction heating furnace, electric furnace or flame furnace where it is melt-spun into a fiber. Before contacting a reel or capstan or other supporting members, the fiber is prime-coated with a baked coating of thermosetting resin, metal coating or inorganic coating to thereby provide a strong fiber for optical communication which is yet to be jacketed with a secondary coating.

An experiment was conducted to produce a glass fiber for optical transmission using the method of this invention in the following manner. The glass-making gases indicated below were supplied through a silica nozzle comprising coaxial pipes as shown in Figure 3(b) and having an outside diameter of 30 mm; NH_3 was supplied through a pipe 31 at a rate of 3 l/min, helium was supplied through a pipe 34 at a rate of 1 l/min, SiH_4 and helium were supplied through a pipe 32 at rates of 0.1 l/min and 1.9 l/min, respectively, helium was supplied through a pipe 35 at a rate of 1 l/min, and CO_2 was supplied through a pipe 33 at a rate of 7 l/min. A silicon nitride pipe around the nozzle was used as a passage through which a mixture of helium and nitrogen was supplied at a rate of 20 l/min. A platinum wire was wound around the silicon nitride pipe and an electric current was passed through the wire to heat the nozzle assembly. The temperature of the nozzle assembly was 1,200°C when no gas was supplied through it. Under these conditions, fine particles of glass were formed, heated to 1000°C in vacuum, held in a carbon dioxide atmosphere at that temperature for 3 hours, and thereafter elevated to 1,450°C to produce an N-doped glass composition having a refractive index of about 1.480. Thereafter, the supply of NH_3 was replaced by a gradual supply of helium gas for producing and sintering fine glass particles. The amount of nitrogen dopant decreased until the final index of refraction of the glass was 1.459. Another experiment was conducted to produce a glass product according to the method illustrated in Figure 1 using a silica nozzle of the type shown in Figure 3(a) wherein NH_3 was supplied through a pipe 31 at a rate of 3 l/min, $SiCl_4$ and helium were supplied through a pipe 32 at rates of 0.1 l/min, and 1.9 l/min, respectively, and oxygen was supplied through a pipe 33 at a rate of 3.5 l/min, and the gases were mixed together within a hot gas derived from a high-frequency (3.5 MHz) plasma. After sintering, a transparent glass product was obtained which had a refractive index of 1.475 adequately higher than that of SiO_2.

[2] Process for the direct formation of a molten SiOxNy glass using NH_3 as a starting gas:

Referring to Figure 4, in the OVPD process illustrated therein, a thin-walled silica tube 41 as a starting member is rotated and reciprocated along the longitudinal axis of the tube under a high-frequency plasma torch 42 that generates a hot plasma flame of inert gas such as helium or argon which is directed against the outside wall of the tube 41. If necessary, the tube may be reinforced by inserting a graphite rod in it. A nozzle 43 directed at the tube 41 supplies jets of a gaseous silicon compound, such as monosilane, trichlorosilane, silicon tetrachloride or silicon tetrafluoride; ammonia

and oxygen and/or a gaseous oxygen compound, such as carbon dioxide or nitrogen oxide, and a mixture of these gases is heated in the plasma flame to produce a soot of SiOxNy glass which is directly deposited as a molten layer on the outside surface of the tube 41. Therefore, transparent nitrogen-doped silica glass (SiOnXy) 44 builds up on the outer wall of the tube 41. In this case, an inert gas such as helium or nitrogen is preferably supplied from the outer periphery of the nozzle 43 so that it encloses the gases mentioned above to provide separation from ambient air. To change the index of refraction of nitrogen-doped silica glass 44 by varying the amount of-nitrogen dopant, the gaseous silicon compound is supplied at a rate that is determined by the desired rate of glass formation, while the ratio of the supply (per given period) of the mixture of ammonia and oxygen and/or gaseous oxygen compound to that of the gaseous silicon compound is held constant, and the ratio of the supply (per given period) of ammonia to that of oxygen and/or gaseous oxygen compound is caused to vary. Such technique is advantageous in that it achieves uniform doping of nitrogen. In the present embodiment, all gases supplied are heated with the plasma flame of inert gas, but instead, the gases flowing through the nozzle 43 may be directly heated by an electric furnace (using a platinum wire) disposed around the nozzle. Instead of rotating and reciprocating the silica tube 41 along its longitudinal axis, the nozzle 43 may be revolved around a fixed silica tube 41 and be reciprocated along the longitudinal axis of the tube.

In a reaction of the type used in this invention where high concentrations of gases are supplied at high temperatures, for example, in a reaction under such conditions that monosilane and a mixture of ammonia and carbon dioxide are supplied at rates of 0.1 l/min and less than 10 l/min, respectively, at 1,000 between 1,500°C, or that silicon tetrachloride and a mixture of ammonia and carbon dioxide are supplied at rates of less than 0.1 l/min and less than 10 l/min, respectively, at 1,100 between 1,700°C, the individual gases are preferably separate from each other when they are jetted from the nozzle 43. It is important that the bonding of silicon and nitrogen is promoted to some extent before the silicon-oxygen bond is formed, and this is achieved by supplying oxygen and/or gaseous oxygen compound from the outer periphery of the nozzle 43. For this purpose, a nozzle 43 comprising two coaxial pipes is employed, and a mixture of gaseous silicon compound and ammonia which is optionally combined with hydrogen and/or inert gas is supplied through the inner pipe, and oxygen and/or the gaseous oxygen compound is supplied through the outer pipe. Alternatively, the nozzle comprises three coaxial pipes, and oxygen and/or gaseous oxygen compound is supplied through an outer pipe, and the gaseous silicon compound and ammonia are separately supplied through the two inner pipes. If necessary, the gaseous silicon compound and ammonia may be mixed with hydrogen and/or an inert gas. In addition, to prevent these gases from reacting with each other and the reaction product from depositing at the tip of the nozzle 43 to reduce the gas flow, one more coaxial pipe may be added to the former type of nozzle so that a gas of high thermal conductivity such as an inert gas, for example helium or hydrogen is supplied between the passage for the mixture of gaseous silicon compound and ammonia and that for oxygen and/or gaseous oxygen compound. In the case of the latter type of nozzle, two more coaxial pipes may be added so that the shielding gas defined above can flow between the passage for the gaseous silicon compound and that for ammonia as well as between the passage for ammonia and that for oxygen and/or gaseous oxygen compound. The advantage of using helium or hydrogen having high thermal conductivity is that it provides a uniform temperature distribution for the gases when they are mixed in the reaction system, thereby achieving the intended even reaction.

The resulting nitrogen-doped silica glass 44 is then freed of the silica tube 41, and its inside as well as outside surfaces are made smooth and clean by a known technique until a perfect cylinder is obtained. It is then mounted on a glass lathe and drawn under heating to collapse the hollow part of the tube to make a preform rod. To the rod, a coating of silica glass doped with titanium dioxide, aluminum oxide, or zirconium oxide is applied by the OVPD process to give a clad optical fiber preform.

Alternatively, a coating of silica glass with or without fluorine dopant may be directly deposited in a molten state on the nitrogen-doped silica glass 44 formed on the outside surface of the tube 41. This is achieved simply by replacing ammonia with a gaseous fluorine compound which is supplied at a given rate and by letting it react with the silica glass 44 at a suitable temperature. The resulting preform is freed of the silica tube 41 and has its inside as well as outside surfaces made smooth and clean to provide a perfect cylinder which is then drawn under heating to collapse the hollow part of the tube to make a clad optical fiber preform.

The preform thus obtained is then subjected to a suitable surface treatment, spun into a fiber and covered with a primary coating to provide a strong fiber for optical transmission which is yet to be jacketed with a secondary coating. The description of the third embodiment is based on the OVPD process, but it should be understood that this invention also permits the use of the MCVD process and VAD process.

To show the advantages of this invention, two experiments were conducted wherein glass preforms for optical transmission were produced according to the process of the third embodiment. In one experiment, a silica nozzle comprising three coaxial pipes was used to supply ammonia, a mixture of silicon tetrachloride and helium, and oxygen. Ammonia was supplied through an inner pipe at a rate of 3 litres per minute, silicon tetrachloride and helium were supplied through an intermediate pipe at rates of 0.1 liter and 1.9 liters per minute, and oxygen was supplied through an outer pipe at a rate of

3.5 liters per minute. These gases were introduced into a hot gas from a high-frequency (3.5 MHz) plasma where they were reacted with each other to provide transparent nitrogen-doped silica glass. The glass had an index of refraction of 1.470 which was adequately higher than that of pure silica glass.

In the other experiment, a silica nozzle comprising five pipes was used to supply the below indicated gases. Ammonia was supplied through the innermost pipe at a rate of 3 liters per minute, helium was supplied through the pipe first from the innermost pipe at a rate of 1 liter per minute, monosilane and helium were supplied through the pipe second from the innermost pipe at rates of 0.1 liter and 1.9 liters per minute, helium was supplied through the pipe third from the innermost pipe at a rate of 1 liter per minute, and carbon dioxide supplied through the outermost pipe at a rate of 7 liters per minute. A mixture of helium and nitrogen was supplied at a rate of 20 liters per minute through the space between the nozzle and a silicon nitride pipe provided coaxially to surround the nozzle. A platinum wire was wound around the silicon nitride pipe to heat the nozzle assembly such that its temperature was 1,400°C when no gas was supplied through it. The resulting soot of SiOxNy glass was built up as a layer of transparent glass on the outside surface of a graphite tube having an outside diameter of 10 mm and a wall thickness of 0.5 mm. As the layer built up, the supply of ammonia was gradually replaced by helium. Then, the graphite rod was burnt out and the inside surface of the tube was washed in hydrofluoric acid to give a cylindrical nitrogen-doped silica glass preform, which was mounted on a glass lathe and exposed to a plasma flame to soften its outside wall. Upon drawing, the hollow part of the tube collapsed to give a rod-shaped optical fiber preform 10 mm in diameter. The core of the preform had a refractive index of 1.478, and the cladding had a refractive index of 1.459.

As is clear from the foregoing description, the process of the third embodiment forms a molten film of SiOxNy glass soot directly on the starting member and obviates the sintering step conventionally required to make transparent glass. This eliminates the possibility of the Si—N bond being displaced by the Si—O bond during the sintering step, and in consequence, the escape of the nitrogen dopant is minimised and the refractive index of the N-doped silica glass can be maintained at a high value.

[3] Process for producing an SiOxNy glass without using NH_3:

The first embodiment shown in Figure 1, can also be performed without using NH_3 as one of the starting materials. In this case, the thin-walled silica tube 11 (which may be reinforced with a graphite rod inserted in it) as a starting member is rotated or reciprocated as shown, and a hot plasma flame 12′ of inert gas such as Ar or N_2 produced by the high-frequency plasma torch 12 is directed against the tube 11. As the hot inert gas issues from the torch, three gases, i.e., a gaseous silicon compound SiH_4, N-supply gas and an oxygen-containing gas, are supplied through a nozzle 13 shown in Figures 3(a) or 3(b), and the mixture of the three gases is heated with said hot inert gas 12 to produce SiOxNy 13′. In Figure 1, a coating of finely divided SiOxNy glass 14 is formed on the starting member.

In a reaction of this type where high concentrations of gases are supplied at high temperatures, for example, in a reaction under such conditions that $SiCl_4$ and a mixture of ClN_3 and CO_2 (each diluted with an inert gas) are supplied at rates of less than 100 cm³/min and less than 1,000 cm³/min, respectively, at 1,150 to 1,800°C, the individual gases must be separated from each other before they enter the reaction system, particularly because the nitrogen halide gas is high explosive. Again, therefore, the nozzle shown in Figure 3(a) and comprising three coaxial pipes 31, 32 and 33 through which separate gases are supplied, may be used as the nozzle 13. Examples of the combinations of gases to be supplied through the three pipes include the combination of a mixture of nitrogen halide and an inert gas (to be supplied through pipe 31), a mixture of a gaseous silicon compound $SiCl_4$, H_2 and an inert gas (supplied through pipe 32), and an oxygen-containing gas (through pipe 33), as well as the combination of a mixture of a gaseous silicon compound $SiCl_4$ and an inert gas (through pipe 31), a mixture of nitrogen halide and an inert gas (through pipe 32) and an oxygen-containing gas (through pipe 33). Another possible combination comprises a mixture of nitrogen halide, a gaseous silicon compound and an inert gas (supplied through pipe 31) and an oxygen-containing gas (supplied through pipe 33). In the last mentioned combination, the pipe 32 is omitted from the nozzle. Again it is to be emphasised that the oxygen-containing gas should be supplied from an outer pipe to ensure at least some Si—N bonding before the formation of the Si—O bond. If the circumstances permit the use of a nozzle of complex construction, the gases mentioned above (those supplied from the central pipe mentioned first, next come those supplied from the intermediate pipe, and those supplied from the outer pipe mentioned last) may be supplied in portions rather than in a single stream. In this case, an oxygen-containing gas may be supplied through the central pipe.

Alternatively, the nozzle shown in Figure 3(b) may be employed so as effectively to prevent gases mixing and reacting with each other right at the discharge end of the nozzle to form fine particles of glass that deposit on the tip of the nozzle to reduce the gas flow. In this case, however, to change the refractive index by varying the amount of nitrogen dopant (the more nitrogen dopant used, the higher the refractive index of SiOxNy), the gaseous silicon compound is supplied at a rate that is determined by the desired rate of glass formation while the ratio of the mixture of nitrogen halide and oxygen-containing gas to the gaseous silicon compound is held constant and the ratio of nitrogen halide to oxygen-containing gas is varied. Such technique is advantageous in that it achieves uniform doping of SiOxNy.

Referring to Figure 5, in the fourth embodiment, a thin-walled silica tube 51 (which may be

reinforced with a graphite rod inserted in it) as a starting member is rotated and reciprocated as shown, and a hot plasma flame of inert gas such as Ar or He produced by a high-frequency plasma torch 52 is supplied with a gaseous silicon compound $SiCl_4$, an N-supply gas and an oxygen-containing gas. The resulting gas mixture is heated with the hot gas to produce fine particles of SiOxNy glass 54 which is melted to form a film of glass 55 on the starting member.

In the fifth embodiment shown in Figure 6, a starting member 81 is rotated and reciprocated while glass-making gases supplied from a nozzle 63 are heated with a combustion flame 62 obtained by burning $(CN)_2$, CS_2 or CCl_4. In Figure 6, 63′ is a pipe through which $SiCl_4$ flows, 63″ is a pipe through which an oxygen-containing gas flows, and 64 is a pipe through which a combustion gas or a mixture of the combustion gas and oxygen gas flows. Here again all gases must be placed in an atmosphere free from any hydrogen compound such as H_2O. It is to be understood that either pipe 63″ or 64 may be omitted since the gas flowing through one pipe can serve the purpose of the gas flowing through the other.

The fine powder of SiOxNy glass 65 formed by the high-temperature reaction is deposited as a glass layer 66 on the starting member. Alternatively, the gases supplied from the nozzle are heated in a hot furnace such as an electric furnace (using a platinum wire). As described above, the construction of the nozzle is such that an inert gas such as hydrogen or nitrogen is supplied from an outer coaxial pipe to provide a separation between air and the gases supplied from inner pipes. The above description of Figures 1 and 5 is based on the formation of a coating of transparent glass on a starting member, but it should be understood that a coating of fine particles of SiOxNy glass is first formed on the starting member before it is sintered to provide transparent glass.

The resulting powder of SiOxNy is then sintered at about 1,450°C which is close to the temperature for sintering undoped SiO_2 glass. This sintering operation differs from the sintering of B_2O_3-, P_2O_5- or GeO_2-doped glass produced by the conventional MCVD method, OVPD or VAD method in that it must be performed in an oxygen-free inert gas atmosphere or in vacuum or in a gas atmosphere containing chloride or nitrogen instead of oxygen. This is because the presence of oxygen at a temperature close to the sintering temperature results in oxidation of nitrogen. Individual fine particles of SiOxNy glass are preferably surrounded by a composition doped with only a small amount of nitrogen and hence close to that of SiO_2, because this results in the production of a sintered product completely free from air bubbles. To provide such a desired product, fine particles of SiOxNy are gradually heated to a temperature lower than the sintering point either in vacuum or an oxygen-free inert gas or chlorine gas, and thereafter, the particles are held in a dry oxygen gas to bring the composition of the superficial part of the particles close to that of SiO_2, followed by sintering in the atmosphere defined above. An effective method for this sintering is the conventional "zone sintering" technique. This way a sintered, transparent glass preform is obtained wherein the content of nitrogen dopant increases to provide a higher refractive index as the radial distance from the center increases.

As in the conventional OVPD process or VAD process, a coating of SiO_2 with or without a fluorine dopant is deposited in a molten state on the outer surface of the preform. Alternatively, said coating is first deposited as finely divided glass which is sintered into transparent glass. To achieve this purpose in the OVPD process as shown in Figure 1 or 5, the reaction may be performed at a suitable temperature with the valve on the N-supply line of this invention being closed or with a fluorine-containing gas being supplied into the N-supply line or the gaseous silicon compound-supply line. In the VAD process, gases to form an outer glass component, for example, a mixture of $SiCl_4$ and O_2, may be blown from an external burner to form a coating of fine particles on the preform.

It is to be noted that the sintered preform obtained by the method illustrated in Figure 1 or 5 is then freed of the starting member 11, and its inside surface is made smooth and clean by reaming, laser treatment, flame treatment, washing in hydrofluoric acid or any other conventional technique to provide a cylindrical glass product, which is optionally set up on a glass lathe and drawn under heating to collapse the hollow part of the cylinder to make a preform rod.

The MCVD process as a sixth embodiment of this invention is hereunder described by reference to Figure 7, in which the outside surface of a silica glass tube 71 that is rotating and translating in axial direction is heated with an oxygen-hydrogen flame 72 (from a burner 72′). A gaseous silicon compound $SiCl_4$, nitrogen halide, e.g. NCl_3, as an N-supply gas, and O_2 as an O-supply gas are supplied into the tube to form fine particles of SiOxNy 93 which are deposited on the inner wall of the tube where they are melted to make a coating of transparent glass 74. Preferably, these gases are introduced into the reaction system separately using a sheathed nozzle such that $SiCl_4$ 75′ is supplied through a pipe 75, NCl_3 76′ through a pipe 76 and O_2 77′ through a pipe 77. Depending on the type of gases used, such sheathed nozzle may be omitted. Here again the amount of nitrogen dopant can be controlled by varying the ratio of nitrogen halide to oxygen gas supplied. Before forming the coating of SiOxNy core glass, a cladding layer comprising, for example, B_2O_3—SiO_2, B_2O_3—SiO_5—SiO_2, B_2O_3—F—SiO_2, P_2O_5—F—SiO_2 or SiO_2 glass, is formed in the same manner as the conventional MCVD process. The silica glass tube having both the cladding and core glass films deposited on the inner wall is then mounted on a glass lathe and drawn under heating (up to 1,800°C) to collapse the hollow part of the tube to make a transparent rod-shaped glass preform.

The PCVD process as a seventh embodiment of this invention is now described by reference to

Figure 8. The PCVD process is performed either under vacuum (using cold plasma) or under atmospheric pressure (using hot plasma), and the following description concerns the use of hot plasma, but it should be understood that this invention also permits the use of cold plasma. A silica glass tube 81 is inserted into a high-frequency coil 82 and rotated and translated along the longitudinal axis as it is heated with a plasma flame 82′ formed within the tube. A gaseous silicon compound $SiCl_4$, N-supply gas such as NCl_3, and O-supply gas such as CO_2 are supplied into the tube to form fine particles of SiOxNy glass 83 which are deposited on the inner wall of the tube where they are melted to make a coating of transparent glass 84. Preferably, these gases are combined at a point near the plasma flame after being introduced into the tube separately such that $SiCl_4$ 85′ is supplied through a pipe 85, NCl_3 86′ through a pipe 86 and CO_2 87′ through a pipe 87. Depending on the type of gases used, such care may not be necessary. Here again the amount of nitrogen dopant can be controlled by varying the ratio of NCl_3 to CO_2 supplied. Before forming the coating of SiOxNy core glass, a cladding comprising the materials mentioned above is formed in the conventional manner. The silica glass tube having both the cladding and core glass films deposited on the inner wall is then mounted on a glass lathe and drawn at a temperature less than 1,800°C to collapse the hollow part of the tube to make a transparent rod-shaped glass preform. The resulting preform cylinder or rod is subjected to a surface treatment to provide a smooth and clean outer surface, and is supplied into a high-frequency induction heating furnace, electrical furnace or flame furnace where it is melt-spun into a fiber. Before contacting a reel or capstan or other supporting members, the fiber is prime-coated with a baked coating of thermosetting resin, metal coating or inorganic coating to thereby provide a strong fiber for optical communication which is yet to be jacketed with a secondary coating.

One example of the production of an optical fiber according to this invention is hereunder described. A silica glass tube (ID 20 mm, OD 25 mm) was set up on a glass and rotated as its outer wall was heated with reciprocating oxygen-hydrogen flame at a temperature in the range of from 1,350 to 1,450°C. In the first stage of the production, $SiCl_4$, O_2, PF_3 and BF_3 were fed into the tube at rates of 100 cc/min, 2,000 cc/min, 50 cc/min and 50 cc/min, respectively, to form a coating of P_2O_5—B_2O_3—F—SiO_2 glass about 1 mm thick on the inner wall of the tube. In the next stage, a sheathed nozzle was inserted into the tube and reciprocated in unison with an oxygen-hydrogen flame (30 mm/min) as $SiCl_4$ was supplied through an inner pipe at a rate of 50 cc/min (diluted with helium supplied at 200 cc/min), ClN_3 was supplied through an intermediate pipe at a rate of 300 cc/min (diluted with N_2 supplied at 300 cc/min) and CO_2 was supplied through an outer pipe at a rate of 200 cc/min (diluted with helium supplied at 300 cc/min). The three gases were kept separate from each other by helium gas supplied at 100 cc/min. When this procedure was repeated for about 5 hours, a coating of SiOxNy having a thickness of about 0.8 mm was formed on the inner wall of the tube. The nozzle was then removed from the tube which was further heated to a temperature less than 1,900°C and drawn to collapse the hollow part of the tube to thereby make a preform having a diameter of 18.9 mm. The resulting preform was heated in a resistance furnace (up to 2,000°C) where it was drawn into a fiber having a diameter of 150 μm. Application of a silicon resin coating gave a fiber having a cladding diameter of 80 μm and a core diameter of 60 μm. The differential refractive index between the core and cladding was 3.0%. The transmission characteristics of the fiber were such that it had a transmission loss of less than 4 dB per kilometer at $\lambda = 0.85$ μm and only 1 dB per kilometer at $\lambda = 1.3$ μ. The concentration of —SiOH radicals was less than 2 ppm.

In another example of the production of a glass for optical transmission using the method of this invention, the glass-making gases indicated below were supplied through a silica nozzle comprising coaxial pipes as shown in Figure 3(b) and having an outside diameter of 30 mm; NCl_3 was supplied through the pipe 31 at a rate of 1 l/min, helium was supplied through the pipe 34 at a rate of 1 l/min, SiH_4 and helium were supplied through the pipe 32 at rates of 0.2 l/min and 1.9 l/min, respectively, helium was supplied through the pipe 35 at a rate of 1 l/min, and CO_2 was supplied through the pipe 33 at a rate of 5 l/min. A silicon nitride pipe around the nozzle was used as a passage through which $(CN)_2$ and O_2 were supplied at rates of 10 l/min and 20 l/min, respectively. A combustion flame was used to heat the nozzle assembly. The temperature of the nozzle assembly was 1,800°C when no gas was supplied through it. Under these conditions, fine particles of glass were formed, heated to 1,000°C in vacuum, held in a nitrogen atmosphere at that temperature for 3 hours, and thereafter elevated to 1,450°C to produce an N-doped glass composition having a refractive index of about 1.483. Thereafter, the supply of NCl_3 was replaced by a gradual supply of hydrogen gas for producing and sintering the fine glass particles. The amount of nitrogen dopant decreased until the final index of refraction of the glass was 1.460.

The advantages of the process of this invention are summarized below:

(1) A glass product can be produced at low cost because it uses as a dopant inexpensive nitrogen-containing compounds, NO_2, CO_2 and O_2 rather than expensive B, P and Ge.

(2) Since the refractive index can be varied greatly according to the content of nitrogen dopant, a preform capable of forming a fiber having a desired numerical aperture can be produced.

(3) The light transmittance of SiOxNy is by no means lower than that of SiO_2. The SiOxNy glass is low in transmission loss at long wavelengths, and is less susceptible to radiation than SiO_2 glass. These features all contribute to the production of a fiber of good characteristics.

(4) SiOxNy has physical properties and chemical durability so close to those of SiO_2 that it is easily drawn to a high-reliability fiber.

(5) The center of the resulting preform has high nitrogen content and is viscous. Unavoidably, the preform under spinning is subjected to temperatures high enough to provide a very strong fiber.

(6) When nitrogen is not supplied in the form of a hydrogen-containing compound such as NH_3 as the nitrogen supplying compound, the gases supplied and the heating source used are anhydrous and, therefore, the process enables the production of a low-loss fiber with a minimum content of

$$-\overset{|}{\underset{|}{Si}}OH$$

radicals.

CLAIMS

1. A process for producing a glass preform for optical transmission which comprises supplying a gaseous silicon compound, a gaseous nitrogen compound and an oxygen-containing gas as starting gases into a combustion flame thereby effecting a reaction in such a manner that the oxygen-silicon bond is formed first and a nitrogen-silicon bond is then formed to produce fine particles of SiOxNy glass and depositing said fine particles in the form of a soot or a transparent glass on a starting member to produce nitrogen-doped silica glass.

2. A process for producing a glass preform for optical transmission which comprises supplying a gaseous silicon compound selected from SiH_4, $SiHCl_3$ and $SiCl_4$, ammonia and an oxygen-containing gas selected from O_2, CO_2 and NO_2 as starting gases into a high temperature zone to form a coating of fine particles of SiOxNy glass on a starting member, and sintering the SiOxNy glass particles in a high-temperature zone to produce nitrogen-doped silica glass.

3. The process according to Claim 1, wherein a gaseous silicon compound, ammonia and oxygen and/or a gaseous oxygen compound are supplied into a high temperature zone where the three gases react with each other to form fine particles of SiOxNy glass, and a layer of the glass particles so formed is directly deposited on a starting member in a molten state to thereby form nitrogen-doped silica glass.

4. The process according to Claim 1, wherein a gaseous silicon compound, nitrogen halide and an oxygen-supply gas are supplied into a high-temperature reaction system to form fine particles of anhydrous SiOxNy glass, a coating of said fine particles of glass being formed on a starting member to produce nitrogen-doped anhydrous silica glass.

5. The process according to Claim 4, wherein the coating of fine particles of anhydrous glass is formed on the starting member in a molten state.

6. The process according to Claim 4, wherein the coating of fine particles of anhydrous glass is formed on the starting member and then is sintered in a high-temperature zone to make nitrogen-doped silica glass.

7. A process according to any of Claims 1 to 6, wherein a gaseous silicon compound and a gaseous nitrogen compound and, optionally, an inert gas are supplied through an inner pipe of a sheathed nozzle, and oxygen and/or gaseous oxygen compound is supplied through an outer pipe of the nozzle, the individual gases supplied being heated in a furnace or by a plasma flame to produce fine particles of SiOxNy glass.

8. The process according to any of Claims 1 to 6, wherein either a gaseous silicon compound or a gaseous nitrogen compound and, optionally, an inert gas are supplied through an inner pipe of a sheathed nozzle, the other compound and, optionally, an inert gas are supplied through an intermediate pipe of the nozzle, and oxygen and/or a gaseous oxygen compound is supplied through an outer pipe of the nozzle, the individual gases supplied being heated in a furnace or by a plasma flame to produce fine particles of SiOxNy glass.

9. The process according to any of Claims 1 to 8, wherein the doping of nitrogen is performed by varying the ratio of gaseous nitrogen compound to the oxygen-containing gas while supplying the gaseous silicon compound at a constant rate.

10. The process according to Claim 8, wherein an inert gas selected from nitrogen and helium is supplied through a passage disposed both between the gaseous nitrogen compound-supply pipe and the gaseous silicon compound-supply pipe and between the gaseous silicon compound-supply pipe and the oxygen-containing gas-supply pipe, to thereby prevent the formation of a reaction product at the exit of the burner as a result of the reaction between the individual gases supplied.

11. The process according to any of Claims 2 or 4, 5 and 6, wherein glass free from OH radicals is produced by performing the sintering in an oxygen-free inert gas atmosphere or in vacuum or in a gas atmosphere containing chlorine instead of oxygen.

12. The process according to Claim 11, wherein the heating is first performed in an oxygen-free

inert gas atmosphere or in vacuum or in a gas atmosphere containing chlorine instead of oxygen, then in an oxygen atmosphere, and the sintering is performed in an oxygen-free inert gas atmosphere or in vacuum or in a gas atmosphere containing chlorine instead of oxygen.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.